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Study of Step-Growth Polymerizations Using Epoxy-Carboxy Reaction

Evidence of Secondary Reactions from Model Study in the Bulk

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SUMMARY

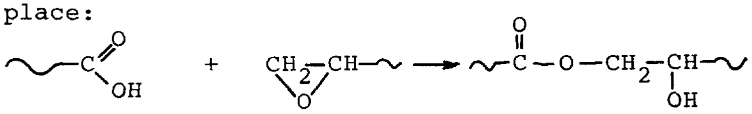
Due to its importance in the fields of block-polycondensation and chemical modification, we carried out a study of the epoxy-carboxy reaction on models(3-phenoxy-1,2-epoxy propane and dodecanoic acid) in the bulk; this reaction was catalyzed either by a tertiary amine (N,N-dimethyldodecylamine) or a chromium chelate (chromium diisopropylsalicylate). Whatever the catalytic system we observed an isomerization of the hydroxy-ester (secondary-primary alcohol) plus transesterification reactions when the catalyst was an amine. The contribution of transesterification reactions is limited when the catalyst is a chromium derivative.

INTRODUCTION

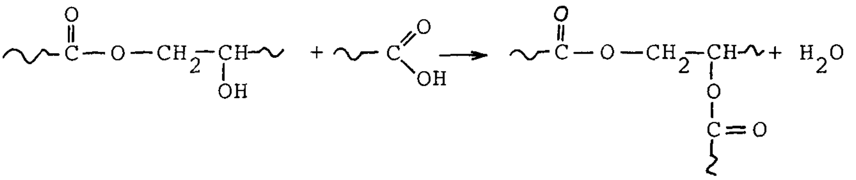
Epoxy-carboxy esterification has many applications in polymer chemistry; however it has been noted that its mechanism is complex and, following numerous studies on model systems, various conclusions have been published (SHECHTER and WYNSTRA (1956); KAKIUCHI and TANAKA (1966); SOROKIN and SHODE(1966) and (1968); FIALA and LIDARIK (1970); UEJIMA and MUNAKATA (1973); MADEC and MARECHAL (1985)). Nearly all these studies focus on kinetic data,which explains why the ultimate stages are rarely described. However a better knowledge of side reactions is more and more necessary to increase the efficiency of the esterification processes.

For this reason we studied the reaction of monoepoxide and monocarboxylic models in the bulk. We followed the evolution of the different species produced by main and side reactions using two analytical techniques: gel permeation chromatography and ^{13}C nuclear magnetic resonance. It will clearly be shown that the characterization of some side species is made possible only by coupling these two techniques throughout all the reaction, even after total consumption of the reactants.

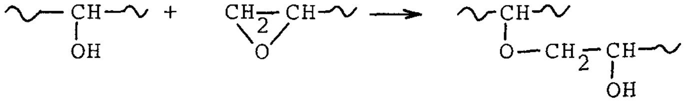
We have already described the kinetical features of the epoxy-carboxy reaction which exhibits several important advantages (MADEC and MARECHAL (1983)). However, as already observed by SHECHTER and WYNSTRA (1956), at least three side reactions can take place:



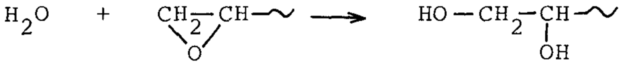
$$\sim C(=O)OH \; + \; \underset{\diagdown O \diagup}{CH_2-CH}\sim \longrightarrow \sim \overset{O}{\overset{\|}{C}}-O-CH_2-\underset{OH}{\underset{|}{CH}}\sim \quad (1)$$



$$\sim\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{OH}{\underset{|}{CH}}\sim + \sim C\begin{matrix}\scriptstyle /\!/O\\ \scriptstyle \backslash OH\end{matrix} \longrightarrow \sim\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{\underset{\underset{\sim}{|}}{\underset{C=O}{\underset{|}{O}}}}{\underset{|}{CH}}\sim + H_2O \qquad (2)$$



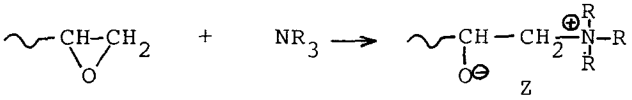
$$\sim\underset{OH}{\underset{|}{CH}}\sim + \underset{\diagdown O \diagup}{CH_2-CH}\sim \longrightarrow \sim\underset{O-CH_2-\underset{OH}{\underset{|}{CH}}\sim}{\underset{|}{CH}}\sim \qquad (3)$$



$$H_2O + \underset{\diagdown O \diagup}{CH_2-CH}\sim \longrightarrow HO-CH_2-\underset{OH}{\underset{|}{CH}}\sim \qquad (4)$$

However, when epoxy-carboxy reaction is base-catalyzed (f.i. a tertiary amine) and carried out in a moderate temperature range, it is usually admitted that the reactions (2),(3) and (4) have no significant contribution.

From kinetic studies on models carried out in solution or in the bulk (MADEC and MARECHAL(1983)), we assumed that tertiary amine and epoxide could interact to give a zwitterion:



$$\sim\underset{\diagdown O \diagup}{CH-CH_2} + NR_3 \longrightarrow \underset{Z}{\sim\underset{O^{\ominus}}{\underset{|}{CH}}-CH_2-\overset{\oplus R}{\underset{R}{N}}-R} \qquad (5)$$

Z can act both as a very efficient catalyst of the reaction, due to its high basicity and as a polymerization initiator of epoxides. With a view to completing the characterization of all side species, we carried out further studies in the bulk between 3-phenoxy-1,2-epoxy propane (PEP) and dodecanoic acid (DA) in stoichiometric conditions and in the presence of two different catalysts: a tertiary amine (N,N-dimethyldodecylamine: DMDA) and a chromium (III) chelate (chromium (III) diisopropylsalicylate: CrDIPS).

EXPERIMENTAL

Dodecanoic acid (DA)(FLUKA; purity 99.5 %) is used without further purification. 3-Phenoxy-1,2-epoxy propane (PEP) (MERCK) is dried over calcium hydride and distilled under nitrogen vacuum; the fraction boiling at 120-122 °C (13.6 Torr) is collected. Purity, determined by chromatography and titration of the epoxy groups is above 99.0 %; N,N-dimethyldodecylamine (DMDA) (FLUKA) is distilled under nitrogen vacuum 82-85 °C (0.1 Torr); purity determined by chromatography is above 99.0 %. Chromium (III) diisopropylsalicylate (CrDIPS) is prepared from chromium (III) triacetate (CARLO ERBA) (I) and diisopropylsalicylic acid (Koch Light Laboratories Ltd)(II).A mixture of I (1.55g), II (2.5g) and ethanol (100ml) is heated to reflux in a reactor equipped with a stirrer and swept by dry N_2. Ethanol and by-products were evaporated under vacuum. GPC showed that CrDIPS is an oligomer ($\bar{M}_n \simeq 2500$) as already assumed by URI(1971) and MATEJKA et al. (1982).3-Phenoxy-1,2-propane diol (DO) is prepared by hydrolysis of PEP (20g) with 1ml H_2SO_4 (95 %) added to 300ml water at 100°C (3h) and is recrystallized in water. 3-Phenoxy-1,2-acetate propane diol (PAPD): DO (5g) and a large excess of acetic acid (50ml) are refluxed for 3h, in the presence of 0.02g $ZnCl_2$; acetic acid and water are evaporated under vacuum. Reactions between PEP and DA are carried out under nitrogen in a PID thermostatted flask fitted with a constant speed stirrer, an inert gas inlet, a sampling device, a thermometer and a condenser. Reactants are heated to the chosen temperature, in stoichiometric conditions, then the catalyst is added.

Analysis: - gel permeation chromatography: chromatograms are recorded on a WATERS 6000 A apparatus; PL-GEL columns (60cm): 50 + 100 Å; elution: THF ($1 ml.mn^{-1}$) - ^{13}C NMR spectroscopy: spectra are recorded on BRÜKER spectrometers (WP80 and WM250) using $CDCl_3$ as solvent (Ref.: $CDCl_3$: 76.9 ppm).

RESULTS AND DISCUSSION

When the reaction between 3-phenoxy-1,2-epoxy propane (PEP) and dodecanoic acid (DA) is carried out in the presence of N,N-dimethyldodecylamine (DMDA), the evolution of the chromatograms (Fig.1) with respect to time shows a first stage corresponding to the formation of a hydroxy-ester (HE). However, secondary peaks can be observed before the complete disappearance of the reactant peaks. According to MATEJKA et al. (1982), these two peaks correspond to products such as 3-phenoxy-1,2-dodecanoate propane diol (DE) and 3-phenoxy-1,2-propane diol (DO), which result from the transesterification of hydroxy-ester HE. In this case transesterification takes place before the epoxy-carboxy reaction is complete. Chromatogram (d) shows that DO can react with DE to give monoester HE.

When the reaction between PEP and DA is carried out in the presence of CrDIPS, GPC chromatograms (Fig.2) show a great reduction of the extent of the transesterification reactions, compared to the base-catalyzed reaction. This is confirmed by the ^{13}C NMR analysis.

However it is worth mentioning that very important information, which did not appear in the chromatograms, was obtained from the ^{13}C NMR spectrum (Fig.3) of the product obtained from PEP-DA CrDIPS-catalyzed reaction corresponding to chromatogram (c) (Fig.2) (no significant transesterification). In fact, we can see three carbons other than those relative to the main structure of HE. These carbons correspond to α and β isomers (secondary and pri-

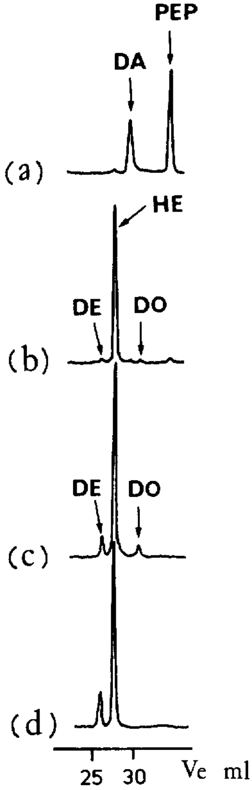


Fig.1- GPC chromatograms of reaction products between PEP and DA in the presence of DMDA ([DMDA]=2.1%molar) (temp. 150°C; (a):t=0; (b):t=0.25h; (c):t=5h; (d):t=31h). (col.:PLGEL 50+100Å-THF:$1 ml.min^{-1}$)

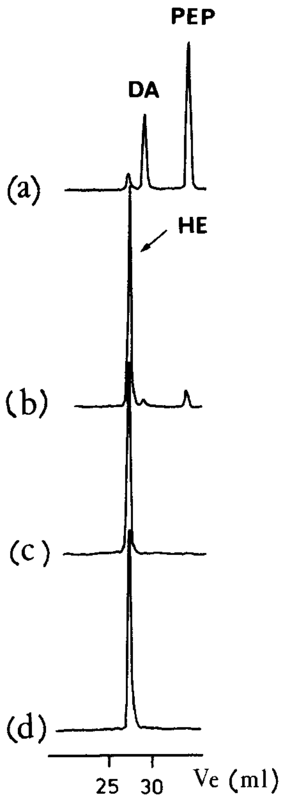


Fig.2- GPC chromatograms of reaction products between PEP and DA in the presence of CrDIPS ([CrDIPS]= 0.05 % molar) (temp. 100°C; (a) : t ≃ 0; (b) : t=0.5h; (c) : t=2h; (d) : t=9.5h). (GPC conditions as in fig.1).

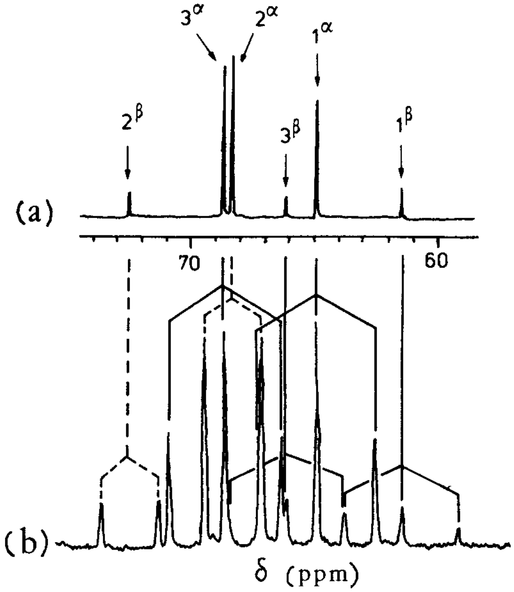
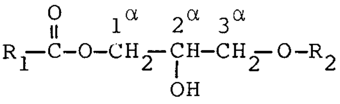


Fig.3- ^{13}C NMR spectra before (a) and after gated decoupling (b) of the product of the PEP-DA reaction corresponding to (c) chromatogram of fig.2. [- - - - -: CH; ——— :CH_2] .

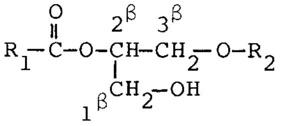
mary alcohols respectively):



$R_1-\overset{\overset{O}{\|}}{C}-O-\overset{1^\alpha}{CH_2}-\underset{OH}{\overset{2^\alpha}{CH}}-\overset{3^\alpha}{CH_2}-O-R_2$

α-isomer

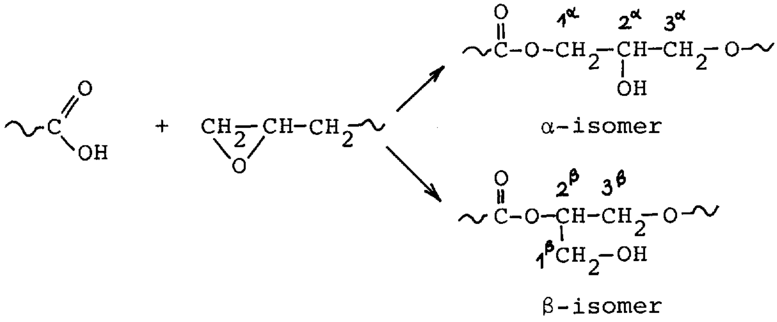
β-isomer



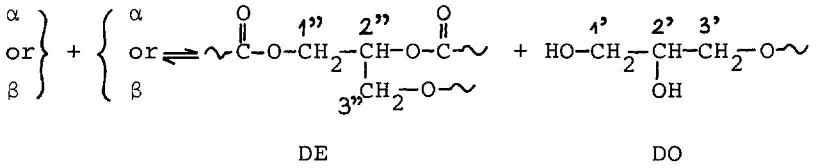
$R_1-\overset{\overset{O}{\|}}{C}-O-\underset{{}_{1^\beta}CH_2-OH}{\overset{2^\beta}{CH}}-\overset{3^\beta}{CH_2}-O-R_2$

The different carbons relative to α and β isomers were assigned from results obtained on closely related species (GAGNEBIEN (1985)). Moreover, they have been confirmed by recording ^{13}C NMR spectra, using gated decoupling sequences (Fig.3). The different carbon chemical shifts and coupling constants (J_{C-H}/ Hz) are reported in table 1; they show clearly that the observed carbons have very close relaxation times, which allows quantitative measurement of the ratio : $\beta/\alpha+\beta$. [In conditions of fig.3: $\beta/\alpha+\beta = 0.14$] .

Thus the global reactional scheme include the main esterification reaction (6) and secondary transesterification reaction (7),whose extent depends on the nature of the catalyst:



(6)



(7)

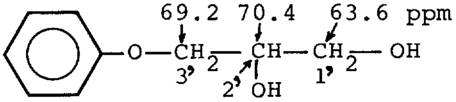
Table 1 - ^{13}C NMR assignments relative to α and β-isomers.

α-isomer				β-isomer			
C n°	δ(ppm)	Integr.	J_{C-H} Hz	C n°	δ(ppm)	Integr.	J_{C-H} Hz
1^{α}	64.95	1.60	147.5	1^{β}	61.5	0.27	144.0
2^{α}	68.35	1.57	145.3	2^{β}	72.6	0.24	147.2
3^{α}	68.7	1.66	144.6	3^{β}	66.2	0.27	146.4

When transesterification takes place (f.i. base-catalyzed reaction) the analysis of ^{13}C NMR spectra (Fig.4) gives rise to the following remarks which fit the GPC chromatograms.

- spectrum (a): only carbons relative to α and β isomers are observed (β/α+β= 0.16).

- spectrum (b): the structures due to transesterification corresponding to DE and DO can be observed. The reduced ratio β/α+β (β/α+β= 0.08) shows that transesterification consumes β-isomer rather than α. The carbons of DO, prepared independently (see exp. part) was recorded with a gated decoupling sequence:



DO

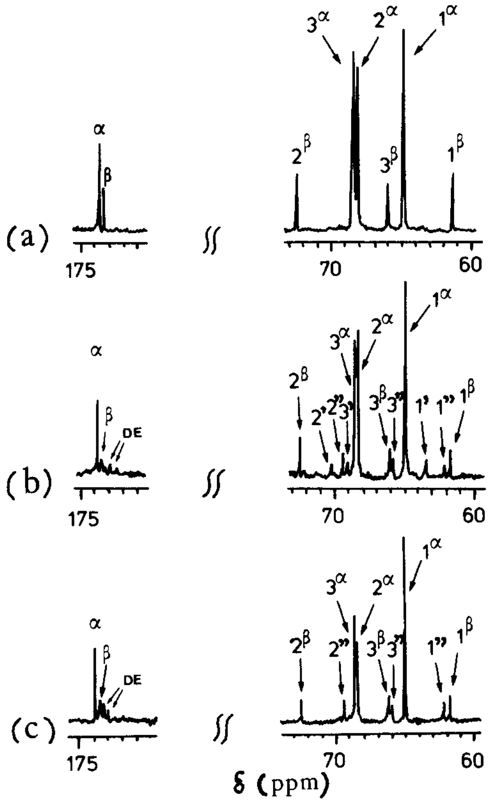


Fig.4- ^{13}C NMR spectra at different stages of the PEP-DA reaction catalyzed by DMDA ([DMDA]= 2.1% molar). Temp.:150°C- Reaction time:(a):0.25h; (b):5h; (c):31h.

This enabled us to assign the carbons of DO in the reaction mixture. The ^{13}C NMR analysis (broad band and gated decoupling) of 3-phenoxy-1,2-acetate propane diol (PAPD) confirms the assignments of the diester (DE) (table 2).

- spectrum (c): it shows the absence of DO. Only α and β isomers and diester DE appear.

Contrary to the amine-catalyzed reaction, the secondary species issued from transesterification reaction are not easily visible on 13C NMR spectrum, even when the reaction is carried out at high temperature (θ=150°C) in the presence of CrDIPS (Fig.5). The absence of transesterification is in relation to the constant value of the ratio β/α+β versus time (β/α+β=0.20). However the contribution of the transesterification reaction increases with increasing reaction temperature (table 3).

Table 2 - ^{13}C NMR assignments relative to diesters: 3-phenoxy-1,2-dodecanoate propanediol (DE) and 3-phenoxy-1,2-acetate propanediol (PAPD).

n° C	1''	2''	3''
DE δ (ppm)	62.2	69.3	66.0
PAPD δ (ppm)	62.0	69.3	65.5

Table 3 - Extent of isomerization versus temperature.

θ °C	100	150
$\frac{\beta}{\alpha+\beta}$	0.14	0.20

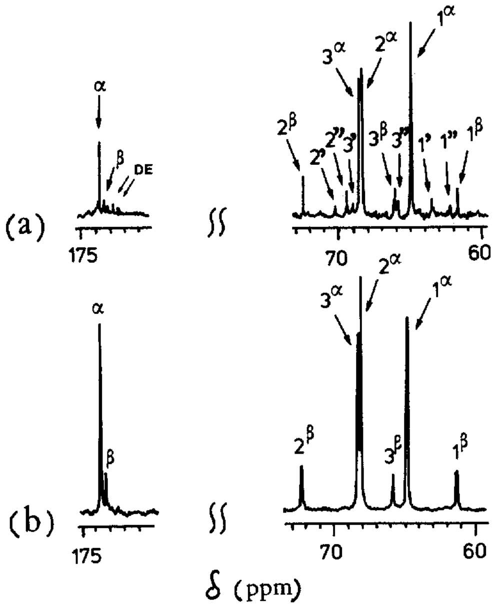


Fig.5- ^{13}C NMR spectra of the reaction mixture corresponding to the heating of PEP and DA. (Temp.: 150°C- reaction time: 5h) - (a): [DMDA] = 2.1% molar; (b): [CrDIPS] = 0.05% molar.

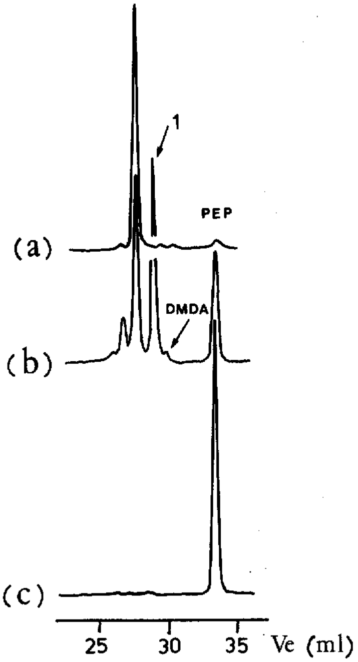


Fig.6- GPC chromatograms of the PEP-DA reaction, in the same conditions as fig.1 (chrom.(a)), of the polymerization of PEP initited by DMDA (θ=120°C; [DMDA]=2.1%molar; t=2h) (chrom.(b)), of the reactional mixture resulting from the heating of PEP in the presence of CrDIPS (θ=120°C; [CrDIPS]=0.05% molar; t=4.5h) (chrom.(c)). Conditions as in fig.1.

The contribution of transesterification reaction is, in all cases, very low compared to that of epoxide polymerization. Even when the reaction is amine-catalyzed, the structures of the epoxidic oligomers corresponding to the specific reaction between PEP and DMDA (ex. peak n° 1 on chromatogram b) are not observed on the GPC chromatograms (Fig.6). It is note worthy that, in the same conditions, no epoxide polymerization is initiated by CrDIPS.

CONCLUSION

This study of a model epoxy-carboxy reaction was carried out in the bulk, in stoichiometric conditions, up to total conversion of reactants in the presence of a tertiary amine (DMDA) or a chromium chelate (CrDIPS). It shows clearly that:

- in the first stage of the reaction, and whatever the catalytic system, two isomers α and β are formed very rapidly corresponding to secondary and primary alcohol respectively.

These were characterized by ^{13}C NMR; $\beta/\alpha+\beta$ increases with temperature.

- in the last stage, transesterification reactions took place when the reaction was amine-catalyzed. The formation of the diester and of the diol has been thoroughly analyzed by ^{13}C NMR, which shows clearly that the diester is formed by transesterification and not by direct esterification as generally assumed in the literature. The contribution of isomer β to transesterification is important. On the other hand the chromium (III) chelate (CrDIPS) catalyses only the isomerization whereas transesterification seems almost non-existent. This observation is of the greatest importance in, for example, the synthesis of block copolymers by epoxy-carboxy reaction.

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